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1999 United States-Latin America-Canada-Caribbean Workshop on Molecular and Materials Sciences: Theoretical and Computational Aspects

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Summary

This workshop brought together advanced doctoral students, research scientists and teaching Faculty members of US, Latin-American, Canadian, and Caribbean institutions to review recent developments in the theoretical and computational aspects of molecular and materials sciences. The emphasis was on theoretical methods and computer programs of general applicability with mid-range computing facilities. The workshop took place at the Instituto de Fisica, Universidad Nacional Autonoma de Mexico, en Cuernavaca, Mexico, on February 24 to 26, 1999.

A total of 49 oral presentations were discussed, with the participation of 44 senior scientists and 39 students. Many of the presentations related to the calculation of properties of materials, and computational methods applicable to them. Among these, presentations were made on the nonlinear optical properties of polymers, metal clusters and inorganic materials of interest in catalysis, epitaxial growth of solid surfaces and their study with ion bombardment, carbon nano foam formation by laser ablation, and the accurate calculation of thermochemical properties. A related area was the computer modelling of compounds of interest in biological systems. Some contributions in these areas involved studies of photosynthetic reaction centers, compounds of importance in bioenergetics, and properties of liquid water.

The workshop was supported, in addition to the Office of Naval Research, by the University of Florida Division of Sponsored Research, and by the Quantum Theory Project, an Institute for Theory and Computation in Molecular and Materials Sciences in its College of Liberal Arts and Sciences. Support was also provided in Mexico by several institutions as listed in what follows.

The following pages contain:
1) Table of Speakers and Titles of Talks;
2) Abstracts of Presentations; and
3) List of Participants (in order of registration).

US-LATIN AMERICAN-CANADA-CARIBBEAN WORKSHOP ON MOLECULAR AND MATERIALS SCIENCES: THEORETICAL AND COMPUTATIONAL ASPECTS.

Cuernavaca, Morelos, Mexico, Febrero 24-26, 1999.

Workshop Organizers

Salvador Cruz, UAM-Iztapalapa, Mexico
David A. Micha, University of Florida, USA
Alejandro Ramirez, UAE-Morelia, Mexico
Jose Recamier, Centro de Ciencias Fisicas, UNAM, Mexico
Alberto Vela, CINVESTAV-IPN, Mexico

Workshop sponsors

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Universidad de Florida Division of Sponsored Research, and Quantum Theory Project, USA
Universidad Autonoma del Estado de Morelos (UAEMor), Mexico
Universidad Nacional Autonoma (UNAM), Mexico

Table of Speakers and Titles of Talks

U.S. - LATIN AMERICA - CANADA - CARIBBEAN
WORKSHOP ON MOLECULAR AND MATERIAL SCIENCES
THEORETICAL AND COMPUTATIONAL ASPECTS

HORARIO	MIERCOLES	JUEVES	VIERNES
8:30 a 9:00	Inauguración		
9:00 a 9:20	Dr. David A. Micha, "First Principles Quantum Molecular Dynamics of Electronic Excitation and Charge Transfer" University of Florida	Dr. Humberto Saint Martín, "An Ab Initio Study of the Hydrolysis Reactions of Neutral and Anionic Mg-Pyrophosphate Complexes in the Gas Phase" Centro de Ciencias Físicas UNAM	Dr. Ilya Kaplan, "Model Potentials and study of binding in small metal clusters" Instituto de Investigaciones en Materiales - UNAM
9:20 a 9:40	Dr. Bernard Kirtman, "New Theoretical and Computational Insights Regarding Nonlinear Optical Properties of Conjugated Polymers and other Quasilinear Materials" University of California, Santa Barbara	Eugene Gamaly, "Carbon nano-foam formation by ultra fast laser ablation" UAM-I	Dra. Graciela Bravo, "Many - Body Effects in Small Au_4 Clusters" Instituto de Física - UNAM
9:40 a 10:00	Dr. James Dufty, "Aspects of Electron Dynamics in the Presence of an Ion" University of Florida	Dr. Ignacio Garzón, "Structure, Electronic and Dynamical Properties of Gold Nanoclusters calculated from Semiempirical Many Body Potentials and Density Functional Theory using Molecular Dynamics Simulation and Evolutive Optimization Methods." Instituto de Física -UNAM	Dr. Agustín E. González, "Colloidal Aggregation with Sedimentation: Computer Simulations" Centro de Ciencias Físicas - UNAM
10:00 a 10:20	Dr. Eduardo Castro, "Estudio Teórico de los complejos de inclusión - oclusión del ácido Hidroxiacetico con la beta - ciclodextrina" Universidad Nacional de la Plata	Dr. Carlos Quintanar, "Density-functional embedding approach to the Mn impurities in NaBr crystals". San Diego Supercomputer Center	Juvencio Robles, "Estudio abinitio de la reactividad y un posible proceso de polimerizacion de un monomero labdatrieno" Universidad de Guanajuato,
10:20 a 10:40	Dr. Luis Mochan, "Energy conservation in surface sum frequency generation" Centro de Ciencias Físicas- UNAM	Mayra Martínez, "Density functional embedding approach to the Mn impurities in NaBr crystals" San Diego Supercomputer Center	María Eugenia Costas, "Purine Derivative Hypoxanthine Physicochemical and Chemical Behavior. The Density Functional Theory Point of View. UNAM
10:40 a 11:00	Dr. Manuel Berrondo, Brigham Young University	Dra. Guillermina Lucía Estiú, CEQUINOR- Facultad de Ciencias Exactas Universidad Nacional de la Plata	Dra. Hai-Ping Cheng, "Novel Surface processes via particle bombardment" University of Florida
11:00 a 11:20	C A	F	E

Cada sesión será: Pláticas de 15 minutos de exposición más 15 minutos de preguntas

HORARIO	MIERCOLES	JUEVES	VIERNES
11:20 a 11:40	Dra. Alicia Jubert, Universidad Nacional de la Plata	Dra. Rocío Jáuregui, "Two photon Raman Scattering and its use for manipulating atomic systems" Instituto de Física- UNAM	Dr. Alejandro Amaya, "Electron capture total cross sections for the system H+ + Ar from 1 to 100 KeV/amu" Centro de Ciencias Físicas -UNAM
11:40 a 12:00	Dr. Alejandro Ramírez, "Theoretical Spectroscopy including Spin-Orbit effects using highly correlated wavefunctions" Facultad de Ciencias -UAEM	Dr. Eugenio Ley, "The Hydrogen Molecular Ion $H+_2$ Inside Spheroidal Boxes With Penetrable Walls" Instituto de Física -UNAM	Dr. Ramón Hernández, "Reaction and inelastic collisions in O_2 ($v>>0$) + $O_2(v=0)$" Centro de Investigaciones en Química -UAEM
12.00 a 12:20	Dr. Sidonio Castillo, "Interaction of small clusters of bimetallics with H_2" UAM-A	Adalberto Corella, "The hellium atom confined within spheroidal boxes" Universidad de Sonora	Dr. John Sabin, "Stopping Powers of Swift Ions Calculated from Molecular Generalized Oscillator Strength Distributions" University of Florida
12:20 a 12:40	Dr. Luis Rincón, "On the interpretation of Molecular Orbital Calculations in Chemical Reactions using Localized Reactant Configurations." Universidad de los Andes, Mérida, Venezuela, Departamento de Química, Facultad de Ciencias	Sergio Mateos, "Polarizability of the confined Hydrogen molecular ion" Instituto de Física - UNAM	Ana Martínez, "Reactions of Cr and Mo atoms and cations with NO: A density functionalstudy". UAM-I
12:40 a 13:00	Dra. Virineya Bertín, "Pb-Pt/A1203 catalyst. Chemisorption properties" UAM-I	Dr. Salvador Cruz, "Properties of the hydrogen molecule confined in a spherical box with penetrable walls" UAM-I	Dr. Iván Ortega, "The affects of molecular relaxation on the description of liquid water" Centro de Ciencias Físicas, UNAM
13:00 a 13:20	Dr. Christof Jung, "Bend vibrations of acetylene" Centro de Ciencias Físicas -UNAM	Dra. Rosa María García, "Manifestaciones de la correlación electrónica en un punto cuántico armónico" Instituto de Física - UNAM	Dr. Jacques Soullard, "Properties of the hydrogen molecule confined in a spherical box with penetrable walls" Instituto de Física - UNAM
13:20 a 13:40	Dr. Michael Zerner, "Some theoretical Studies on the Photosynthetic Reaction Center" University of Florida	Dr. Dennis Salahub, "DFT, H-bonds and Aspects of Enzyme Mechanics," Montreal University	MESA REDONDA
13:40 a 16:20	C O M I D A		

HORARIO	MIERCOLES	JUEVES	VIERNES
16:20 a 16:40	Dr. Renato Contreras, "Non-Local (Pair Site) Reactivity from Second Order Density-Response Functions" Universidad de Chile	Dr. Carlos Bunge, "Driving RISC processors close to peak performance" Instituto de Física - UNAM	
16:40 a 17:00	Dr. Alberto Vela, CINVESTAV	Xavier Periole "Nuevo métodos de extracción de potenciales efectivos catión-agua para simulaciones numéricas" Facultad de Ciencias	
17:00 a 17:20	Gabriel Cuevas, "Reactividad Química" Instituto de Química -UNAM	Dr . Alejandro Frank, Centro de Ciencias Físicas -UNAM	
17:20 a 17:40	Eva M. Ziemniak "Epitaxial grwth of the strutures on the surfaces"	Rocío Meza, "Cinética y Mecanismo de la Adición Conjugada de Arilmercaptanos a Ciclohexenona" CINVESTAV	
17:40 a 18:00	Dr. Samuel B. Trickey, "Summary of Some Recent Developments in Density Functional Theory" University of Florida	Vicente Ortíz, "Applications of Electron Propagator Theory to Exotic Molecular Anions" Kansas State University	
18:00 a 18:20	CAFE	Dr. David Dixon, "Computational Thermochemistry: Reliable Predictions" Computational Thermochemistry: Reliable Predictions	
18:20 a 18:40	Gerardo Cisneros, S.G.I.		

Abstracts of Presentations

FIRST PRINCIPLES QUANTUM MOLECULAR DYNAMICS OF ELECTRONIC EXCITATION AND CHARGE TRANSFER: A DENSITY MATRIX THEORY [1]

David A. Micha

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Gainesville FL 32611, USA

Abstract

Three fundamental problems in a first principles quantum molecular dynamics will be described, as well as our proposed solutions. They are: (1) the calculation of state-to-state transition probabilities and expectation values of properties for systems with complicated sequences of electronic rearrangements, from a knowledge of eikonal functions; (2) properly accounting for the translational motion of electrons moving with the nuclei to avoid spurious couplings of atomic states; and (3) solving the coupled differential equations for the time-dependent interactions of fast electrons and slow nuclei while avoiding numerical difficulties associated with the coupling of very different time scales.

Our solution to the first problem is based on the introduction of eikonal representations of molecular wavefunctions and density matrices, and the calculation of probabilities and expectation values with sums over initial values of positions and momenta of bundles of trajectories. The second problem requires a rethinking of atomic function expansions and of methods of calculating one- and two-electron integrals for electronic structure. This has been done introducing linear combinations of traveling atomic orbitals. The third problem has been solved with the introduction and implementation of a "relax-and-drive" method for propagating many-electron density matrices, suitable for large time steps.[1-3]

The theory will be illustrated with examples of collision induced electronic energy and charge transfer, and light emission, in ion-atom and ion-surface collisions at kinetic energies ranging from a few eV to thousands of eV.[4-7]

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1. J. M. Cohen and D. A. Micha, J. Chem. Phys. 97, 1038 (1992).

2. D. A. Micha, Intern. J. Quantum Chem. 51, 499 (1994)

3. D. A. Micha, Intern. J. Quantum Chem. 60, 109 (1996)

4. D. A. Micha and K. Runge, Phys. Rev. A 50, 322 (1994)

5. D. A. Micha and E. Q. Feng, Computer Phys. Comm. 90, 242 (1994)

6. K. Runge and D. A. Micha, Phys. Rev. A 53, 1388 (1996)

7. H. F. M. DaCosta, D. A. Micha and K. Runge, J. Chem. Phys. 107, 9018 (1997)

Electron Dynamics in the Presence of an Ion

J. Dufty
Physics Department, University of Florida

Abstract

Some problems of current interest to the plasma physics community are noted. These entail the development of efficient and effective means to simulate electron dynamics at high temperatures. Some present attempts at modifying classical MD to accommodate the inherently quantum ion-electron interaction are discussed. Problems, both fundamental and practical, are noted. The objective is to solicit input from the participants using related methods in quantum chemistry, solid state, and warm condensed matter.

Energy conservation in surface sum frequency generation

W. Luis Mochán[1], V. L. Brudny[2], Andrei V. Petukhov[3], Jesús Maytorena
Córdova[1], and Bernardo S. Mendoza[4]

[1]Centro de Ciencias Físicas, Universidad Nacional Autónoma de México,
Cuernavaca, Mor., México

[2]Departamento de Física, Universidad de Buenos Aires,
Buenos Aires, Argentina,

[3]Research Institute for Materials,
Catholic University of Nijmegen, The Netherlands

[4]Centro de Investigaciones en Optica, León, Gto., México

Abstract

Three wave mixing processes, such as optical sum frequency, differ-
ence frequency and second harmonic generation (SFG/DFG/SHG), at
the surface of centrosymmetric systems have become a very useful tool
in surface science, as the bulk contribution to these processes is strongly
symmetry-supressed. We show that the usual Manley Rowe (MR) energy
conservation relations for three wave mixing are not applicable within
these media, as they lead to paradoxical and mistaken results. We find
that this is due to a contribution to the energy flow besides the usual
Poynting vector. Thus, absorption and emission of electromagnetic en-
ergy at the incoming and outgoing frequencies in SFG/DFG processes
may be spatially separated. Taking account of this additional flow, we
obtain novel symmetry relations for the bulk susceptibility and a set of
restrictions on the surface response. These relations are model indepen-
dent and may be used in theory and in data analysis. A part of the
nonlinear surface susceptibility turns out to be completely determined by
the bulk response, while the remaining part does obey the usual MR rela-
tions. For specific models models of surface SFG and DFG we verify the
generalized energy conservation relations, we obtain explicit expressions
for the additional energy flow and we interpret them in terms of convec-
tive energy transport for conductors and of magnetic dipolar and electric
quadrupolar contributions for dielectrics. As an application we obtain the
bulk induced surface susceptibility of homogeneous isotropic semiinfinite
conductors and dielectrics, and we show that the values for some of the
phenomenological parameters commonly used to described surface three
wave mixing are fixed by the energy conservation relations.

Theoretical Spectroscopy including Spin-Orbit effects using highly correlated wavefunctions.

A. Ramírez-Solís

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Cuernavaca, Morelos. 62210 MEXICO.

Relativistic effects are very important and cannot be neglected for molecules containing heavy atoms. The Darwin and mass-velocity corrections are now routinely included in most Relativistic Effective Core Potentials commonly used. However, the Spin-Orbit (SO) effects are rather important for heavy elements and can be taken into account explicitly only after the molecular valence wavefunctions have been obtained. The theoretical spectroscopic results for many molecules containing transition metal atoms are wrong, even qualitatively, if these effects are not included at the zeroth order description. Examples of this situations can be found in the $CuCl_2$ and AgF molecules.

An efficient two-step algorithm to obtain accurate fine-structure (Ω) energies and wavefunctions built upon the $|\Lambda S\Sigma>$ basis of purely electronic states will be presented. The first step involves the determination of the $|\Lambda S\Sigma>$ states using large CASSCF calculations to obtain accurate molecular orbitals for each electronic state followed by large multireference MP2 (CIPSI) calculations. Then a spin-orbit pseudopotential $W^{SO}(A)$ for each atom A is extracted to accurately reproduce the lower part of the atomic spectrum. These are used in the construction and diagonalization of an effective hamiltonian (electronic + SO) for the whole molecule through the CIPSO algorithm.

Bend vibrations of acetylene

C. Jung, C.C.F. UNAM Cuernavaca
M. Jacobson, MIT Boston
H. S. Taylor, USC Los Angeles
R. Field, MIT Boston

Acetylene is one of the smaller polyatomic molecules for which extremely accurate measurements of the vibrational spectrum for the electronic ground state are available. In this molecule there is very little coupling between stretches and bends, accordingly the pure bend vibrations can be isolated. Recently a spectroscopic Hamiltonian has been fitted for the bend vibrations (M. Jacobson et al., J. Chem. Phys. 109, 121 (1998)). This Hamiltonian is the starting point for a semiclassical explanation of the dynamics of the bend vibrations. Originally the system has 4 degrees of freedom, a doubly degenerate cis mode and a doubly degenerate trans mode. However the Hamiltonian has two conserved quantities and they allow the reduction of the system to one with 2 degrees of freedom. With the methods of nonlinear dynamics we investigate the classical motion of this reduced system. In particular we obtain the skeleton of the important periodic orbits. Because the reduced system has 2 degrees of freedom there are two important chains of periodic orbits forming this skeleton. By a comparison with the quantum mechanical wave functions on the reduced configuration space we can assign most of the quantum mechanical states as excitations along these skeleton orbits. This allows an assignment of the states by quantum numbers also in polyad numbers and energy regions where the normal modes have lost their meaning and where the classical phase space contains large scale chaos. This assignment via the skeleton of important classical periodic orbits indicates immediately which type of motion is dominant for the formation of each quantum state. Finally we lift the motion from the reduced phase space into the original fulldimensional phase space to obtain the connection between motion on the reduced configuration space and the motion of the atoms in the usual position space. At the lower ends of the polyads we obtain mainly local bend motion of one H atom, at the upper end of the polyads mainly counter-rotating motion of the two H atoms. In the middle of the polyads we obtain more complicated motion which connects continuously local bend motion

with counter-rotating motion. These links are given by the two important chains of periodic orbits mentioned above. In total, our procedure gives an amazingly simple, complete and closed picture for the dynamics of a system which initially had been considered to be too complicated to allow for any complete analysis of the dynamics.

Some Theoretical Studies on the Photosynthetic Reaction Center

Michael C. Zerner
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Gainesville, FL 32611 USA

Photosynthesis is the process in which light energy is converted into enough chemical energy to synthesize sugars and starches from atmospheric carbon dioxide. It is the principle source of the biomass on earth and is responsible for creating an oxidizing atmosphere above the surface of the earth. Much is known about the chemistry that follows the initial photochemical event, but the first millisecond that follows the absorption of light is not well understood, and is still surrounded by controversy. The crystallographic structures that are becoming available today make this process amenable to detailed theoretical study.

In this seminar I will describe first the electronic spectroscopy of chlorophyll and describe why chlorophyll is a particularly good choice to be the central molecule in this process. I will describe also the excited states of the "special pair", a dimer of chlorophylls, and show why this again is a unique structure, guaranteeing that the dimer possess the lowest energy excited state, and thus efficient energy transfer from the antenna chlorophyll to the reaction center. We will present calculations on the antenna systems observed in bacteria, an inner-ring of 16 chlorophylls and an outer ring of 8, showing how nicely these energy levels overlap for efficient energy transfer. Finally, we will examine the six chromophores (four bacteriochlorophylls and 2 bacteriopheophytin molecules in the bacteria R. viridis and present a model of how the energy that went into exciting the special pair is used to transfer an electron from the special pair to the distant pheophytin, and to begin the sequential chemistry needed to fix atmospheric carbon dioxide and synthesize the molecules necessary for life as we know it.

References:

M.A. Thompson, J. Fajer and M.C. Zerner, "A Theoretical Examination of the Electronic Structure and Spectroscopy of Model Bacteria Chlorophyll Dimers", J. Phys. Chem. 94 (1990) 3820;

M.A. Thompson and M.C. Zerner, "The Effects of a Polarizable Medium on the Charge Transfer States of the Photosynthetic Reaction Center", J. Am. Chem. Soc. 112 (1990) 7828;

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M.A. Thompson, M.C. Zerner and J. Fajer, "A Theoretical Examination of the Electronic Structure and Excited States of the Bacterial Chlorophyll-b Dimer from R. Viridis", J. Phys. Chem. 95 (1991) 5693;

M. G. Cory and M. C. Zerner, "Calculations of the Electronic Affinities of the Chromophores Involved in Photosynthesis," J. Amer. Chem. Soc. (1996), 118, 4148–4151.

M. G. Cory, M. C. Zerner, X. H. Hu and K. Schulten, Electronic Excitations in Aggregates of Bacteriochlorophylls, J. Phys. Chem. , in press

SITE ACTIVATION IN A HARD-HARD INTERACTION FROM MODEL STATIC DENSITY RESPONSE FUNCTIONS

Renato Contreras
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Casilla 653- Santiago, Chile.

Abstract

A general formalism to deal with site activation in a hard-hard interaction is presented. The model is derived from first and second order static density response functions, that go beyond the local approximation on the softness kernel and its first derivative with respect to the number of electrons. The resulting model is applied to the gas phase interaction between the ambident CN and a proton, as a prototype for hard-hard reactions. The model introduces the analysis of reactivity parameters around a virtual transition state structure, which gives a better raectivity picture that the one obtained from the static model developed around the isolated structure. At first order, the hard site (Nitrogen) displays a linear response upon perturbation induced by a hard electrophile,whereas the response at the soft (Carbon) site is non-linear. This result which may be rationalized in terms of a local HSAB principle, agree well with the observed reactivity pattern displayed by this system.

# ESTUDIO COMPUTACIONAL DE LAS PREFERENCIAS CONFORMACIONALES DE ARSOCANOS SUSTITUIDOS.

Cuevas, G.;[1] Madrid, G.;[1] Salazar-Parra, M.;[2] Cea-Olivares R.[1]

1. Instituto de Química, U.N.A.M. Circuito Exterior Ciudad Universitaria. México, D.F. 04510.

2. Escuela de Ciencias Químicas. Universidad La Salle. Benjamín Franklin 47. México D.F., 06140.

La preferencia conformacional por el isómero bote-silla del 5-cloro-1-oxa-4,6-ditiarsocano y del 2-cloro-1,3,6-tritia-2-arsocano, así como de sus cationes derivados por eliminación del cloruro correspondiente tiene un origen estereoelectrónico causado por una interacción de tipo $n_X \rightarrow \sigma^*_{As-Cl}$ (X = O,S). Este hecho es congruente con las evidencias experimentales disponibles y se estableció en el marco de la *Teoría de los Funcionales de la Densidad* a nivel *Becke3LYP/6-31G(d,p)*, analizando la densidad electrónica mediante la teoría topológica de átomos en moléculas de Bader.
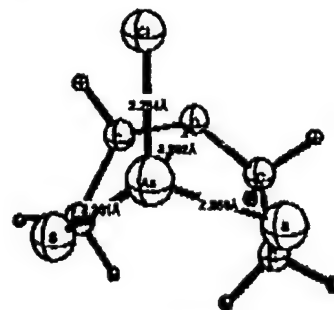
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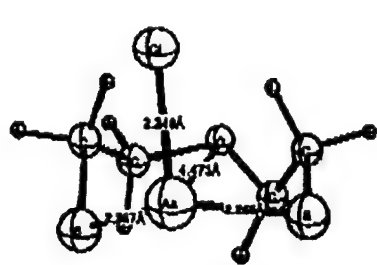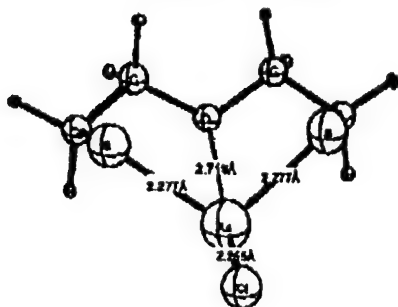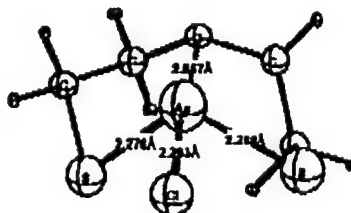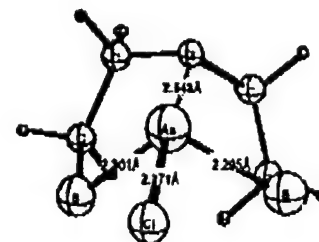

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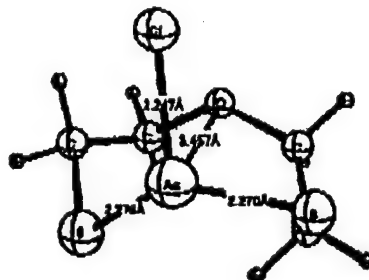
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Epitaxial Growth of the Structures on Surfaces

Eva. M. Ziemniak[1,3], Christof Jung[1,2] and Francois Leyvraz[1,2]

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[2]Centro de Ciencias Fisicas, Cuernavaca, UNAM
[3] University of Bochum and Bielefeld, Germany

Abstract

Searching for the materials and process conditions

Typical ab-initio computations can propose PES (Potential Energy Surface) for specific materials (and epitaxial process) which is defined on the grid points, thus very unefective and intensive in use of computer resources. Accordingly it must be restricted to a certain region and fitted by simpler functions. In our approach we need complete PES including periodical short-range potential, diffusion barriers, precursor and modifier states and corrugation by the growth of overlayer. In addition Schwoebel-Ehlich Effect is included by adsorption of multilayers. Therefore flexibel fit of PES and effective approach is in our case necessary. We can vary the symmetries of the substrat in addition to the parameters controlling dynamical classical process of scattering, trapping, diffusion, hopping, and adsorption by chosen substrat temperature and energy losses along the trajectory of projectile approaching the surface. Only relative values of the parameters characterising the beam, substrat and dynamic process are used for predictions of the growth and morphology of interest. This in principle may be realized by several materials and process conditions which can be found afterwords i.e. in the literature (some cases are discussed) or identified as access for new experiments. The perspectives for incorporating the methods of scattering and chaos theory can be explored.

Silicon Graphics en la Química Computacional

Gerardo Cisneros

Silicon Graphics, S.A. de C.V.

En esta plática se describe el estado actual de la línea de productos de Silicon Graphics, su impacto en el mercado del cómputo científico de alto rendimiento tanto global como académico, de investigación y nacional, y la participación de Silicon Graphics en los diferentes segmentos de aplicación de la química computacional.

An Ab Initio Study of the Hydrolysis Reactions of Neutral and Anionic Mg-Pyrophosphate Complexes in the Gas Phase

Humberto Saint-Martin[†*] and Luis E. Vicent[†,‡]

The most ubiquitous reaction in metabolic processes is the hydrolysis of phospho-anhydryde bonds, and the simplest compound with such bonds is the diphosphoric acid, which is both biologically relevant and amenable to theoretical calculations. Furthermore, there is compelling evidence that the biologically active pyrophosphate species is the hydrated complex with magnesium $[Mg \cdot (H_2O)_4 \cdot P_2O_7]^{2-}$. This evidence is based on the analysis of the complexes that are present in the solution under physiological conditions.

In this work *ab initio* calculations were performed to study the stability of various anhydrous and monohydrated complexes of Mg^{2+} with pyrophosphates and or-thophosphates at the self-consistent-field (SCF) and second-order perturbation (MP2) levels of the theory, using a 6-31+G** basis set with diffuse and polarization functions. New equilibrium geometries were found for the anhydrous Mg-pyrophosphate complexes, that modify previous estimates of the isomerization energies. It is found that the interaction with the water molecule stabilizes the pyrophosphates with respect to the metaphosphate-containing complexes, thus modifying the reaction energies to such an extent that the isomerization results endothermic and non-spontaneous for the dianionic complex. However, the hydrolysis reactions are all exothermic and spontaneous. Moreover, it is found that the water molecule readily breaks upon interacting with the dianionic complex, producing a hydroxide anion: $H_2O + [Mg \cdot P_2O_7]^{2-} \rightarrow [HO \cdot Mg \cdot HP_2O_7]^{2-}$, and the resulting dianionic complex is much more stable than the isomer with a metaphosphate. It is shown that this result is consistent with both an associative and a dissociative mechanism for the hydrolysis.

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Structural, Electronic, and Dynamical Properties of Gold Nanoclusters calculated from Semiempirical Many Body Potentials and Density Functional Theory using Molecular Dynamics Simulation and Evolutive Optimization Methods *

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Structural, electronic and dynamical properties of isolated gold nanoclusters are studied by combining several theoretical and computational techniques. First, the lowest energy structures of Au_n, (n=38,55,75) nanoclusters are determined by unconstrained dynamical and evolutive (genetic/symbiotic) optimization methods, using a Gupta n-body potential. A set of amorphous structures, nearly degenerate in energy, are found as the most stable configurations. Some crystalline or quasicrystalline isomers are also minima of the cluster potential energy surface with similar energy. First principles calculations using density functional theory confirm these results and give different electronic properties for the ordered and disordered gold isomers. A common neighbor analysis technique is used to classify the structures of the amorphous gold nanoclusters and to characterize the short-range order in such disordered structures. Distorted multilayer icosahedral order is found as the most representative of the amorphous isomers for the three sizes investigated. Second, the vibrational properties and thermal stability as a function of the cluster temperature is investigated using constant-energy molecular dynamics and the Gupta n-body potential with parameters fitted to the most stable cluster energies and geometries obtained by density functional theory. The entropy effect at finite temperatures is studied by calculating the cluster free energy using its harmonic vibrational frequencies. A comparison of the free energy at finite temperatures for amorphous and crystalline structures shows a slight enhancement of the stability of the disordered with respect to the ordered cluster structures. Different isomerization behavior is found for the ordered and amorphous cluster isomers of a given size. The calculated cluster melting temperatures for the gold nanoclusters with n=38,55, and 75 is around 400 K.

Density-functional embedding approach to the Mn impurities in NaBr crystals

Marco Garcia Horsman, Mayra Martinez y Carlos Quintanar

abstract

We have performed density functional calculations for three 19-atom clusters, two 25-atom clusters and one 18-atom cluster each embedded in a Madelung potential that takes into account the long range electrostatic interactions of the ions lattice of a NaBr crystal. Two of them model bulk crystalline NaBr; the others model an M^{2+} impurity trapped in a cubically symmetric crystalline electric field (CEF) site of the NaBr host. One of the latter has the NaBr bulk interatomic distance, while in the others relaxation of the Br atoms around the metallic impurity has been considered. The 18-atom cluster models a relaxed Mn-impurity Na-vacancy system. All of our calculated clusters have a Na site at the center, and they all include at least first and second nearest-neighbor host atoms. In the center of the doped clusters the Mn impurity replaces the missing Na ion. The electronic structure of the embedded impurity ion in its local environment was computed self-consistently by means of all-electron density functional theory (DFT) techniques. We have examined the lattice relaxation around the impurity, and calculated the hyperfine coupling constants. The results for the Mn electronic structure, and for the hyperfine coupling constant are in agreement with experimental results using electron paramagnetic resonace measurements.

Density-functional embedding approach to the Mn impurities in NaCl crystals

MAYRA MARTINEZ Y CARLOS QUINTANAR

abstract

We have performed density functional calculations for three 19-atom clusters, two 25-atom clusters and one 18-atom cluster each embedded in a Madelung potential that takes into account the long range electrostatic interactions of the ions lattice of a NaCl crystal. One of the three 19-atom, and one of the two 25-atom clusters models bulk crystalline sodium chloride; the others model an Mn^{2+} impurity trapped in a cubically symmetric crystalline electric field (CEF) site of the NaCl host. One of the latter has the NaCl bulk interatomic distance, while in the others relaxation of the Cl atoms around the metallic impurity has been considered. The 18-atom cluster models a relaxed Mn-impurity Na-vacancy system. All of our calculated clusters have a Na site at the center, and they all include at least first and second nearest-neighbor host atoms. In the doped clusters the Mn impurity replaces the sodium ion at the center. The electronic structure of the embedded impurity ion in its local environment was computed self-consistently by means of all-electron density functional theory (DFT) techniques. We have examined the lattice relaxation around the impurity, and calculated the hyperfine coupling constants. The results for the Mn electronic structure, and for the hyperfine coupling constant are in agreement with experimental results using EPR measurements.

Two-photon Raman Scattering and its usefulness in manipulating single atoms

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The effects of laser beams in the internal and motional states of atoms has been the subject of much theoretical and experimental work. In particular, laser cooling techniques provide methods to reduce first and second order Doppler shifts in ultrahigh resolution spectroscopy and allow for the possibility of controlling the positions and momenta of a collection of atomic particles to within the limits imposed by quantum fluctuations. Two photon Raman scattering has been used by NIST group to cool a single trapped ion into its quantum ground state of motion for approximately 95% of the time . Not long ago, the same group reported the experimental generation of nonclassical motional states of a ion in a radiofrequency Paul trap has been reported . Thermal, Fock, coherent and Schrödinger-cat like states of motion at the single atom level were produced.

Due to spontanoeus decay, the loss of motional coherence of these quantum states was expected to take a long time with respect to the time needed to generate and detect them. However, experimental results showed decoherence rates that, *e. g.*, prevented the experimental generation of Schrödinger cat states in Paul traps with a separation greater than about 85 nm. The purpose of this work is to study by nummerical simulations some of the effects which can lead to such a decoherence. We first consider the simplest simulation that includes the essential features of the experimental arrangements reported in the literature for the generation and detection of Schrödinger cats. Then, we analize the consequences on the evolution of the system of introducing one by one some elements which make more realistic the simulation. In particular we consider nonlinear effects in the coupling of the center of mass coordinates with the laser field, the finite spontaneous decay rate of the internal energy state $|0>$ which couples the two hyperfine internal

states $|1>$ and $|2>$ in the two-photon Raman transitions, different values of the Rabi frequencies g_{10} and g_{20}, the time-dependent character of the electromagnetic field of the Paul trap, random fluctuations of such a field, and the three dimensional character of the motion. The quantum evolution of the ion internal and center of mass degrees of freedom is studied by means of amplitude equations derived from Schrodinger equation. The limitations of such an approach are also discussed.

HYPERFINE SPLITTING OF ATOMIC HYDROGEN IN ALPHA-QUARTZ REVISITED.

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Abstract

The measurements of the isotropic and anisotropic hyperfine splittings of atomic hydrogen in alpha-quartz [1] were not completely and satisfactorily explained on the basis of diverse models of confined atoms [2-6]. In this work the system is revisited on the basis of a new model in which the hydrogen atom is confined in a prolate spheroidal box with penetrable walls. Agreement between the calculated and experimenta hyperfine splitting is achieved for reasonable size and barrier parameters of the model.

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THE HELIUM ATOM CONFINED WITHIN SPHEROIDAL BOXES

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The direct variational method is used to estimate some interesting physical properties of the He atom and Li+ ion within impenetrable spheroidal boxes. A comparative investigation of the ground-state energy, pressure, polarizability, dipole and quadrupole moments whit those of He atom inside boxes with paraboloidal walls is made [1]. The overall results show a similar qualitative behavior. However, for Li+ there are quantitative differences on such properties due to its major nuclear charge, as expected. The trial wave function is constructed of two hydrogenic wave functions adapted to the geometry of the confining boxes.

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THE HIDROGEN MOLECULAR ION H_2^+ INSIDE SPHEROIDAL BOXES

WITH PENETRABLE WALLS

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The hydrogen molecular ion H_2^+ under compression was investigated using a model of its confinement inside spheroidal boxes with impenetrable walls [1-3], including calculations of the hyperfine splitting [1], the electronic and vibrational properties [2] and the polarizability and quadrupole moment [3]. It was recognized that such a model exaggerates the effects of compression for the properties evaluated in [2-3], and also that its adaptation to explain the hyperfine structure of atomic hydrogen in α-quartz shows quantitative inconsistencies with the measured values [1]. This has been a motivation for the development of alternative models, in which the confinement effect is less rigid. This contribution introduces a model of confinement inside spheroidal boxes with penetrable walls, using the potential

$$V(\xi,\eta) = -\frac{2Z_A e^2}{R(\xi+\eta)} - \frac{2Z_B e^2}{R(\xi-\eta)} + \frac{\hbar^2}{2\mu}\frac{F\xi^2}{\xi^2-\eta^2}\Theta(\xi-\xi_o)$$

in terms of prolate spheroidal coordinates with a focal distance R for the electron, where Z_A and Z_B are the electric charge numbers of the nuclei located at the focii. The first two terms correspond to the respective nucleus-electron Coulomb energies. The last term involves the reduced mass μ of the nuclei, vanishes inside the box with a major axis $R\xi_o$, and acts as a barrier outside the box. The Schrödinger equation for such a potential admits separable solutions inside ($1 \leq \xi \leq \xi_o$) and outside ($\xi_o \leq \xi \leq \infty$) the box, with common functions in the hyperboloidal and azimuthal φ coordinates coinciding with those of [1]. The functions of the ellipsoidal coordinate $\Xi(\xi \leq \xi_o)$ and $\Xi(\xi_o \leq \xi)$ are of the type introduced in [1] and of the Jaffe type, respectively. The continuous matching of these functions and their derivatives at the boundary $\xi = \xi_o$ determines the electron energy eigenvalues. The systematic evaluation of the properties of the hydrogen molecular ion in different situations of confinement is under way and will be discussed and illustrated.

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Properties of the hydrogen molecule confined in a spherical box with penetrable walls

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Abstract

The effect of pressure on various properties of molecular hydrogen is analyzed through a simple confinement model whereby the hydrogen molecule is enclosed by a spherical box with finite barrier potential height (V0) at its boundary. The total molecular energy as a function of box-radius and barrier height is calculated through the Floating Spherical Gaussian Orbital scheme using a single-gaussian orbital representation for the electrons. The pressure dependence of polarizability, internuclear distance and Raman shift is calculated for V0 =0 , 0.25 , 1.0 and infinity (atomic units) . Comparison with available experimental measurements on molecular hydrogen under high pressure (liquid and solid) gives supporting evidence on the adequacy of the use of a padded molecule-in-a -box model for this problem.

Manifestaciones de la correlación electrónica en un punto cuántico armónico

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Las funciones de onda así como los niveles de energía de dos electrones que interaccionan en un punto cuántico armónico han sido calculados de manera analítica con la aproximación de dos parábolas y con el método WKB [1]. La correlación se presenta tanto en correcciones de niveles de energía así como en el desplazamiento espacial de la función de onda del movimiento relativo, a medida que la razón entre la repulsión Coulombiana y el potencial de confinamiento varía. Toda esta información es útil en el cálculo de la función dieléctrica. Figuras representativas y cálculos numéricos serán presentados.

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NUEVO METODO DE EXTRACCION DE POTENCIALES EFECTIVOS CATION-AGUA PARA SIMULACIONES NUMERICAS

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Se presenta un nuevo método de extracción *ab initio* de potenciales efectivos por pares. para reproducir la interacción catión-agua en simulaciones numéricas. Se derivaron potenciales efectivos para los cationes Li^+, Na^+, K^+, Be^+, Mg^{2+}, Ca^{2+}, Rb^+ y Sr^{2+} incluyendo los efectos de no-aditividad y los de polarización inducidos por las interacciones catión-agua y agua-agua. Estos potenciales son comparados con los potenciales empíricos obtenidos por Aqvist [J. Phys. Chem. **94** (1990) 8021] que fueron ajustados para reproducir resultados experimentales.

Los potenciales efectivos obtenidos con la técnica de exploración-ETI (energía total de interacción) resultaron ser los mas cercanos a los de Aqvist y son probados en simulaciones de dinámica molecular para todos los sistemas de cationes en solución acuosa. Los resultados estructurales y energéticos obtenidos de estas simulaciones se encuentran en buen acuerdo con resultados experimentales, en particular proporcionando energías libres de hidratación (ΔG) que concuerdan bien éstos. Este método de extracción está idealmente adaptado para la extracción de potenciales efectivos para estudiar sistemas moleculares con condiciones geométricas restringidas (como sitios metálicos catáliticos en enzimas) con simulaciones numéricas, sean éstas de Monte Carlo o de dinámica molecular.

CINETICA Y MECANISMO DE LA ADICION CONJUGADA DE ARILMERCAPTAÑOS A CICLOHEXENONA.

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Las reacciones de adición nucleofílica a sistemas alfa,beta-insaturados han jugado un papel muy importante en la formación de nuevos enlaces carbono-carbono. Más aun si eśtos involucran heteroatomos. La adición de mercaptanos catalizadas por bases a este tipo de sistemas es una reacción importante en procesos biosintéticos así como en síntesis. Hasta ahora no existen reportes de adiciones conjugadas de tioles a sistemas conjugados en donde la reacción se lleva a cabo sin la intervención de base alguna. Esto llamó nuestra atención e hizo que quisieramos conocerla a detalle.

Se eligió como sistema alfa,beta-insaturado a la ciclohexenona y como nu cleofilo una serie de tioles aromáticos para-sustituidos, estos últimos son: NO2, H, OCH3, CH3,Br, Cl. Las reacciones se llevaron a cabo en 1,4-dioxano. De la literatura se conoce que el ataque nucleofilico de tipo Michael sobre compuestos carbonilicos alfa,beta-insaturados es promovido por nucleofilos ricos en electrones, sorprendentemente en este caso la reacción con p-nitrotiofenol procedió más rápidamente (k=3D4.1 x 10 -4 L/mol s a 99 oC, en 1,4-dioxano, utilizando 1H RMN), que aquella en donde el sustitu yente es el grupo OMe (k=3D1.03 x 10 -4 L/mol s, determinada bajo las mismas condiciones.

Ya que las propiedades electrónicas del sustituyente no explican este comportamiento se decidió determinar las blanduras locales (mediante calculos de tipo ab initio utilizando TFD) del átomo nucleofílico de los tioles, en este caso el átomo de azufre, y se observó que en realidad los susitutyentes en posición para afectar directamente a la blandura del átomo de azufre. Así,

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el p-nitrotiofenol resulta ser el tiol que posee el átomo de azufre más blando y por lo tanto el que reacciona más rapidamente sobre el carbono beta de la ciclohexenona, el carbono más blando del sistema alfa,beta-insaturado.

Computational Thermochemistry: Reliable Predictions

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A clear revolution in science has taken place over the last two decades. This revolution is based on the utilization of high performance computers (now massively parallel) to solve the complex equations such as the Schrodinger equation for electronic motion which describe natural phenomena. Both software and hardware developments have contributed to this revolution. We will describe how very high level computational chemistry can be used to predict molecular properties focussing on heats of formation. The thermochemical calculations are based on extrapolating CCSD(T) energies obtained from the correlation-consistent basis sets, up through augmented quadruple-z, to the complete basis set limit. Core/valence corrections were obtained from basis sets designed to recover such effects. Spin-orbit corrections to the atomization energies, zero point energy corrections, and relativistic corrections also need to be included. We will discuss the accuracy of such calculations and their application to a variety of compounds.

MANY-BODY MODEL POTENTIALS AND THEIR APPLICATION TO METAL CLUSTER STABILITY

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We discuss the physical nature of many-body forces (the exchange, induction and dispersion origin) in atomic clusters and solids. The many-body decomposition of the binding energy of the BeN and LiN clusters calculated at the MP4 electron correlation level [1] indicates that the BeN clusters are unstable in the additive 2-body approach and are stabilized by the attractive 3-body interactions, while in the LiN clusters the 3-body forces are the destabilizing factor, these clusters are stabilized by the 2-body interactions. The methodology [2, 3] of constructing many-body potentials with parameters fitted to ab initio calculated potential surfaces are described. One of application of ab initio model potentials are the molecular dynamics (MD) simulation studies. The advantages of using ab initio model potentials in the MD simulation are demonstrated on the example of the simulation of the thermal behavior of different isomers of the Ag6 cluster [4]. Ab initio model potentials are useful also in studies of a nature of binding in metal clusters [3,5]. The analysis of the exchange and dispersion contributions to constructed model potentials for Li3 and Be3 clusters allows to elucidate the nature of binding in these clusters.

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Many-Body Effects in Small Au_n Clusters

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The *many-body* (MB) effects of the $Au_{n=3-6}$ isomers recently optimized with the perturbational Möller-Plesset of *2nd*-order (MP2) ab initio method have been obtained within the same level of ab initio calculations. Dimers, trimers, tetramers, and pentamers components of the analyzed structures were calculated and the component energies included in the total energy expansion $E(n) = \sum_i^{MB} E_i(n)$. As in other metal clusters, the $non-additive$ contributions for the Au_n series are not small. Competition of *additive* and $non-additive$ effects is discussed in relation to geometrical parameters like compactness of the structures and gain in stability. The general behaviors are similar to other metal series investigated, and therefore fit very well with the theoretical explanations based on MB-effects, supporting their origin.

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Colloidal Aggregation with Sedimentation: Computer Simulations

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A computer simulation of colloidal aggregation, that takes into account the coupling and interplay of the aggregation phenomena with the sedimentation that takes place once the aggregates have reached a critical size, is designed much in the same spirit as previous simulations on aggregation done by the author[1,2]. By means of extensive computer runs of the algorithm, it is shown that for high strengths of the downward drift the system crosses over to a regime different from diffusion-limited colloidal aggregation, for which there is an increase of the fractal dimension and a speeding up of the aggregation rate. It is also shown that ϕ^*, the volume fraction at which the system first gels, increases considerably with respect to the zero drift case. All these results are in good agreement with the available experimental data[3].

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Purine Derivative Hypoxanthine Physicochemical and Chemical Behavior.
The Density Functional Theory Point of View.

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Hypoxanthine belongs to a family of heterocycles that are subject of actual research in several fields. In order to advance in the knowledge of the hypoxanthine physicochemical properties, a Density Functional Theory level study of this purine derivative was performed. In this, full geometry optimization and total molecular energy calculations for all the possible isomers and tautomers in the different protonation states were carried out. Several molecular and electronic structure properties for the more favored isomers and tautomers in all the protonation levels were calculated. Also, thermodynamic stability studies of the heterocyclic protonic transfer processes and isomerism and tautomerism were carried out. Finally, the theoretical IR vibrational spectra and their characterization were obtained for the favored forms. From the study, several theoretical trends were found, which have been successfully employed to account for some features of the experimental physicochemical and chemical behavior of hypoxanthine.

Novel Surface Processes via Particle Bombardment

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Abstract

We report our work on large scale molecular dynamics (MD) simulations of silicon surface modification, via various projectile particles such as highly charged ions, atoms, or clusters. We will discuss simulation models for studying processes that are characteristically different. Our investigations include energy redistributions, fragmentation, surface modification, and the influence of energy dissipation into the electronic systems. Physical properties of the systems during the collision processes are fully analyzed.

ELECTRON CAPTURE TOTAL CROSS SECTIONS FOR THE SYSTEM $H^+ + Ar$ FROM 1 TO 100 KeV/amu

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Charge exchange process in the collison of a proton beam and an argon target gas has been the subject of considerable experimental effort. In view of the rather wide discrepancies appearing in the literature of this inelastic process at low energies, it is worth to consider it from a theoretical approach. The two-centre atomic orbital close-coupling method has been extensively used for studying ion-atom collisions in the low to intermediate impact energy region. For this energy range, where the velocity of the projectile is of the same order as that of the active target electrons, various states strongly coupled play an important role in the process. This makes the close-coupling method a natural choice to account for the dynamics of the collision. We present a close-coupling semiclasical description for the electron capture for the system $H^+ + Ar \rightarrow H + Ar^+$ in the 1 - 100 Kev/amu energy range. We use a tempered atomic base. The atom is considered in the base state initially. We show electron capture probabilities as a function of the impact parameter and projectile energy. The total cross sections are compared with experimental data from the literature.

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Reaction and inelastic processes in the collision
$$O_2(v >> 0) + O_2(v = 0)$$

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Abstract

A reduced dimensionality model is used to study the reaction $O_2(X^3\Sigma_g^-, v >> 0) + O_2(^3\Sigma_g^-, v' = 0) \rightarrow O_3(X^1A_1) + O(^3P)$ by means of time–dependent and time–independent quantum–mechanical methods. State–selected probabilities and rate constants are obtained for the reactive process as well as for the inelastic collision in which the vibrationally excited oxygen loses one or more quanta. It is found that the experimentally observed jump in depletion rates above a critical value of v could be partially explained by the vibrational relaxation rather than reaction. Reaction only becomes important for relatively high translational energies and therefore the calculated rates are too small at the temperatures of interest. It is concluded, however, that the reaction saddle point region in the potential energy surface plays a crucial role in the enhancement of vibrational relaxation.

short title: Studies of $O_2(v >> 0) + O_2(v = 0) \rightarrow O_3 + O$

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Stopping Powers of Swift Ions Calculated from Molecular Generalized Oscillator Strength Distributions

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In swift ion scattering problems, the Bethe Surface,[1]= which is the Generalized Oscillator Strength (GOS) distribution as a function of energy and momentum transferred "embodies all the information concerning the inelastic scattering of charged particles by an atom or molecule within the first Born approximation"[2]. For example, a cut through the Bethe surface at zero momentum transfer is the dipole oscillator strength distribution. Present technology makes it possible to fabricate oriented samples, so that the directional characteristics of the Bethe surface have also become of interest. For al= l but the simplest systems, calculation of the entire Bethe surface is impossible. It is, however, possible to calculate the GOS corresponding t= o specific transitions. This talk will deal with calculation of the GOS's for several low lying transitions of CO in the polarization propagator approximation. The directional characteristics of the GOS's will be discussed, as will the accuracy of the results and the sensitivity of inclusion of correlation at various levels.

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The Effects of Molecular Relaxation on the Description of Liquid Water

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The assumption that the water molecule is rigid has been extensively used, and is certainly the norm in numerical simulations of aqueous systems. There is however experimental evidence that in the condensed phases an elongation of the OH bond occurs, both in liquid [1] and in ice [2]. There is also theoretical evidence that collective effects allow for the distortion of the water molecule in clusters as small as trimers [3] and that this effect is substantial for larger clusters as pentamers and hexamers [4]. It is therefore possible that a very common assumption is not so sound for the condensed phases and could be responsible for the difficulties encountered in the simulations of liquid water with very refined *ab initio* potentials, that include polarizability and many-body nonadditive effects. On the other hand, the currently available *ab initio* potentials were fitted to a pair interaction surface with a dimerization energy of -5.8 kcal/mol, whereas the theoretical limit has recently been set at -4.94 ± 0.02 kcal/mol [5], and this discrepancy could also account for the aforementioned difficulties.

In this work we explore both possibilities, searching for an improvement in the description of liquid water, with models that can be extended to thermodynamical conditions where the current potentials have not been totally successful [6]. We adjusted a rigid water surface of 651 dimers, 113 trimers and 15 tetramers, and a flexible potential to the above surface plus 154 deformed monomers, 168 intramolecularly relaxed dimers, 101 trimers and 18 tetramers. The *ab initio* monomer and dimer surfaces were computed with an aug-cc-pVQZ basis set, whereas the three- and four-body nonadditive contributions were computed with a 6-311++G(2d,2p) basis set. The electron correlation energy was included by means of many-body perturbation theory up to the second order (MP2), and the nonadditive contributions were counterpoise corrected. We compare the results of numerical simulations of liquid water at ambient conditions made with the two models.

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Reactions of Cr and Mo atoms and cations with NO: A density functional study.

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The interaction of Cr and Mo atoms and cations with NO was investigated with the all-electron linear-combination-of-Gaussian-type-orbitals Kohn-Sham density functional theory. Several local minima on different potential energy surfaces were found. The lowest minima for CrNO and CrNO+ are doublet bent and triplet linear structures with binding energies of 61.0 and 43.2 kcal/mol, respectively. The lowest minima for MoNO and MoNO+ are bent structures on the doublet and singlet potential energy surfaces with binding energies of 94.5 and 64.7 kcal/mol, respectively. Correlation diagrams of the Kohn-Sham orbitals for the initial stages of the reaction and for the most stable products are presented. These diagrams allow one to predict qualitatively the relative stability of the different reaction products. For the mechanisms of the reaction, charge transfer processes are suggested. The rate coefficient for the reaction Cr + NO obtained from the calculated molecular data is in good agreement with the observed value.

Proton stopping power in molecular Hydrogen under different pressure conditions.

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Abstract

The molecule-in-a -box model is used to simulate the effect of pressure on the electronic density and mean excitation energy of molecular hydrogen.We use the Floating Spherical Gaussian Orbitals (FSGO) representation for the molecular orbitals and develop an ab initio calculation of the molecular energy and structure -hence allowing for electronic and nuclear redistribution- as a function of the confinement volume (pressure) for H-2 enclosed in a hard spherical box. Accordingly, proton electronic stopping cross sections are calculated for H-2 under different pressure conditions. Stopping cross sections are evaluated within the Orbital Local Plasma Approximation (OLPA)/FSGO implementation of the kinetic theory of stopping .

A systematic reduction of the stopping cross section and a shift of the stopping curve maximum towards higher projectile energies are observed as pressure increases.

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